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(54) Title: **BASIC SUSPENSION, ITS PREPARATION AND PROCESS FOR PAPER DEACIDIFICATION**

(57) Abstract: Basic suspension wherein oxides, hydroxides, carbonates, or their mixture, in the form of particles having determined dimensions are suspended in the appropriated solvents, are described. Processes for the preparation of the above said suspensions and of the suspended particles are also described together with the uses of the suspensions in processes for paper deacidification and/or porous materials consolidation.

BASIC SUSPENSION, ITS PREPARATION AND PROCESS FOR PAPER DEACIDIFICATION

Field of the invention

The present inventions refers to basic suspensions which, thanks to their physico-
5 chemical properties, can annul the acidity present in papers, which depends on
the paper production processes, on the environment pollution, and on the usage of
acid inks as, for example, in the modern books.

State of the art

It is well known how the presence of acidity in paper is the main responsible of its
10 degradation with consequent loss of a lot of important information and in particular
of historically important documents.

The acidity, which is present particularly in modern paper, forms during the paper
manufacture, it is also a consequence of the use of acid inks (which are very
common especially in the last centuries) or because of the adsorption of acid
15 pollutants which are present in the air.

Many different techniques and products have been studied or developed in order
to eliminate acidity from paper and published documents (paper de-acidification).
Unfortunately, up to now, the problem is far to be satisfactorily solved, and the
specialists are intensively looking for new products capable of annulling the acidity
20 present in paper.

Calcium, magnesium, and barium hydroxide aqueous solutions have been widely
used for many decades, but, unfortunately, they had often induced not desirable
side effects, because of their strong alkaline conditions; with subsequent
depolymerization of cellulose.

Non aqueous deacidification processes have also been proposed. In Smith R.D., Mass Deacidification at the Public Archives of Canada in Conservation of Library and Archive Materials and the Graphic Arts, Butterworth Ed., London, 1987 the use of magnesium alkoxide deacidification solutions (Wei T'o method) is described; another method widely used is the Bookkeeper method which is based on the application of suspended MgO that, subsequently converted in magnesium hydroxide, forms the alkaline reservoir. Unfortunately, these methods use chlorofluorocarbon (CFC) solvents. Alternatively, some solvent mixtures have been recently experimented, as thrielyne (90%) and methanol, but all of them are harmful.

Despite of its scarce usage, calcium hydroxide is an excellent deacidifying agent. Calcium hydroxide is physico-chemically friendly to most of papers and, once converted to calcium carbonate, works efficiently as alkaline reservoir. In IT 1.286.868 (in the name of the same Applicant) it is reported that suspensions of calcium hydroxide could be used to consolidate mural paintings and to deacidify paper. However, the calcium hydroxide suspensions in organic solvent described in this document were obtained from lime and the particle size distribution was quite broad and larger than several micrometers. Smaller particles were around 0.5 microns, 80% were greater than 1 micron. This originated two problems: firstly, kinetic stability was good but not excellent for some application procedures, for example spraying; secondly, because of particle sizes, a white glaze (or spots) on the treated surfaces could form.

Large calcium hydroxide particles showed a poor adhesions and penetrability into the cellulosic fibres.

Deacidifying agents must ensure good adhesion with fibres, so that the alkaline reservoir acts efficiently. Therefore, according to physico-chemical features of cellulose, particles with a surface charge density are preferred. Both these requirements are ensured by the use of particles smaller than micron size.

5 Summary of the invention

The present invention refers to basic suspension wherein the suspended particles have determined dimensions, moreover the invention refers to process for the preparation of the suspensions and of the suspended particles and to the use of the suspension in processes of paper deacidification and porous materials
10 consolidation.

Detailed description of the invention

The present invention makes it available basic suspension which allow the overcoming of the problems connected with paper acidity.

The suspension according to the inventions are preferably suspensions of basic
15 oxides or hydroxides (which are capable of forming carbonates when in contact with the CO₂ of the air or to form, once adsorbed on the treated material, a reservoir of basicity stable for long periods of time) or basic carbonates or their mixture.

Particularly preferred according to the invention are the oxides, hydroxides or
20 carbonates of alkali or earth-alkali metals or also other analogous compounds having basic properties.

Examples of compounds suitable for the suspensions according to the invention are: Li₂O, Na₂O, K₂O, MgO, CaO, SnO, SnO₂, PbO, Pb₂O, Pb₂O₃, BiO, Bi₂O₃, Sb₂O₃, LiOH, NaOH, KOH, Mg(OH)₂, Ca(OH)₂, Al(OH)₃, Sn(OH)₂, Sn(OH)₄,

Pb(OH)₂, Bi(OH)₃, Sb(OH)₃, Li₂CO₃, Na₂CO₃ decahydro, Na₂CO₃, K₂CO₃, MgCO₃, CaCO₃, PbCO₃, anhydro and basic, Bi₂O₂CO₃ or their mixtures.

Particularly preferred according to the invention are the suspensions of Mg(OH)₂, Ca(OH)₂, Sn(OH)₂.

- 5 The preferred suspending solvents are chosen in the group consisting of: water, ethyl ether, acetone, alcohols, and their mixtures.

Among the alcohols particularly preferred are: methanol, ethanol, 1-propanol, 2-propanol, butanol, pentanol, and their mixtures.

- Particularly preferred are suspension of the Ca(OH)₂ hydroxide in 1% (w/w) in
10 water and 99% in 1-propanol (or 2-propanol).

- The dimensions of the hydroxide particles in suspension play also a crucial role in the suspensions according to the invention. In fact, such particles must be capable of entering the fibres of the materials to treat, linking with them, without covering effect over the written text since this would produce a not desirable aesthetically
15 effect. Large particles need longer time to penetrate in depth, but the fast volatilisation of used organic solvents does not usually allow it. Therefore, a strict control of particle size is essential before the application.

- Particularly preferred are suspensions according to the invention wherein the suspended particles have dimension comprised between 10nm up to 2µm, more
20 preferably between 50nm up to 500nm.

The suspensions according to the invention have a concentration of suspended particles in the solvent preferably comprised between: 0.1-50 g/L more preferably between 1-25 g/L.

Especially preferred is a concentration of: 10 g/L.

The suspensions according to the invention can be obtained by vigorous stirring of the particles to be suspended in the appropriate solvent (or solvents mixture), if necessary with the aid of a sonicator or ultra-sonicator or with the aid of a homogeniser.

- 5 The particles to be suspended, having the desired measures, can be obtained by high temperature homogeneous phase reaction, heterogeneous phase reaction (slaking of oxides), and by mixing two water in oil microemulsion obtaining a low solubility salt in nanosized aqueous core.

The first process consists in reacting solutions of the appropriate reagents (for
10 example a solution of an hydroxide as NaOH and a solution of a chloride as CaCl₂) at high temperature (about 90°C) under stirring.

The solutions to be reacted can be obtained by solving the reagents in a solvent chosen in the group consisting of: water, a solution of diols or a mixture water/diols (the reagents can be solved both in the same or each one in a different solvent
15 chosen from the above said group).

The preferred diols are C₁₋₆ alkane diols as, for example, 1,2 ethandiol or 1,2 propandiol.

The suspension obtained after reaction at high temperature and containing the formed particles is cooled down to room temperature under N₂, the supernatant
20 solution is eliminated and the suspension is washed to eliminate secondary reaction products and concentrated in vacuum to form a paste which can be suspended again in the desired solvent amount.

According to the slaking of oxides process the oxide is slaked in pure water, the obtained hydroxide paste is mixed with an alcohol under vigorous stirring and sonicated or homogenised.

Alternatively, according to known techniques, two water in oil microemulsions are prepared wherein the aqueous phase containing salts, when the two microemulsions are mixed precipitation takes place wherein the nanosized dimensions of the aqueous drops impose limited growth of particles.

Given the above said, examples of suspensions according to the invention are reported hereinafter in order to better illustrate the invention:

10 **Example 1**

Calcium hydroxide micro-particles have been obtained by slaking CaO powder in pure water, at room temperature:

- CaO powder 10 g
- Water 30 g

15 Successively, suspensions have been prepared by mixing the calcium hydroxide paste with alcohol, under vigorous stirring, and have been sonicated for 30 minutes with an ultra-sonicator for further reducing the particle size and obtaining a complete dispersion of the calcium hydroxide agglomerates. A homogeniser system, for preparation of some hydroxide dispersions, can also be used.

20 **Example 2**

Calcium hydroxide micro-particles have been obtained by slaking CaO powder in water/alcohol mixtures, according to the following proportions:

- CaO powder 1 g
- Water 5 g

- 1-propanol 25 mL

The metal oxide/water/alcohol mixture, after 30 minutes of sonication or vigorous stirring has been left to rest at least 8 hours. Suspensions have been prepared by mixing the calcium hydroxide paste, after filtration, with alcohol, under vigorous stirring. Suspensions have been sonicated for 30 minutes with an ultra-sonicator for further reducing the particle size and obtaining a complete dispersion of the calcium hydroxide agglomerates. A homogeniser system, for preparation of some hydroxide dispersions, was also necessary.

Example 3

Calcium hydroxide nanoparticles, from homogeneous phase reaction, have been achieved by mixing a NaOH aqueous solution with a CaCl_2 aqueous solution. They were previously heated up to a selected temperature (around 90 °C), under continuous stirring and keeping the temperature of the mixture constant within ± 1 °C; the supersaturating degree was kept in the range 2-10. Aqueous $\text{Ca}(\text{OH})_2$ suspension was allowed gradually reaching the room temperature under a nitrogen atmosphere to avoid the $\text{M}(\text{OH})_2$ carbonation. The supernatant solution was discarded and the remaining suspension was washed five times with water to reduce the NaCl concentration below 10^{-6} M. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was controlled by the AgNO_3 test. The suspension was then concentrated in vacuum at 40 °C up to a weight ratio $\text{M}(\text{OH})_2/\text{water}$ of 0.8, that is the same of the standard slaked lime paste. Dispersions have been prepared by mixing 10g of the calcium hydroxide paste with 1L of alcohol, under vigorous stirring, and/or by using a homogeniser.

Example 4

Calcium hydroxide nanoparticles, from homogeneous phase reaction, have been obtained by mixing a NaOH aqueous solution with a CaCl_2 diol solution (i.e. 1,2 ethandiol or 1,2 propandiol). Diol solution was previously heated up to a selected temperature (around 150°C), under continuous stirring and keeping the temperature of the mixture constant within $\pm 1^\circ\text{C}$; the supersaturating degree was in the range 2-10. The NaOH aqueous solution was added dropwise to diol solution keeping the temperature around 150°C . The $\text{Ca}(\text{OH})_2$ water/diol suspension was allowed gradually reaching the room temperature under a nitrogen atmosphere to avoid the $\text{M}(\text{OH})_2$ carbonation. The supernatant solution was discarded and the remaining suspension was washed five times with water to reduce the NaCl concentration below 10^{-6} M. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was controlled by the AgNO_3 test. Then, water/diol suspension was washed several times with 2-propanol to remove diol solvents. Successively, solutions were concentrated in vacuum at 40°C up to a weight ratio $\text{M}(\text{OH})_2/\text{water}$ of 0.8, that is the same of the standard slaked lime paste. Dispersions have been prepared by mixing 10g of the calcium hydroxide paste with 1L of alcohol, under vigorous stirring, and/or by using a homogeniser.

Example 5

Two water in oil microemulsions have been obtained.

C_{12}E_4 surfactant solutions in cyclohexane have been prepared and used as oil phase in the microemulsion. These solutions have been mixed with NaOH (0.1M) and CaCl_2 (0.05M) aqueous solution.

Microemulsion (water in oil) composition is:

- $C_{12}E_4$ 0.15 g (0.2M)
- Cyclohexane 1.15 g
- NaOH (0.1M) and $CaCl_2$ (0.05M) aqueous solution 25 μ L (w=2)

5 Water/surfactants molar ratio ranging (molar ratio w=water/surfactant) from 1 to 5.

Aqueous solution was added to oil phase/surfactant solution by a microsyringe.

The preparation was held at 15°C. Similar isotropic, transparent, and stable systems, were obtained in a wider temperature range, 15-25°C. Microemulsions have been equilibrated at 15°C for 10 days. Crystallization processes took place
10 within the confined volume of the microdroplets. Synthesized particles, after filtration, washing, and drying have been dispersed in nonaqueous solvents, by vigorous stirring and/or with the aid of a homogeniser.

Example 6

Solution of Igepal CO 520 in cyclohexane (0.15M) has been prepared and mixed,
15 respectively, with an aqueous solution of NaOH (0.5M) and with an aqueous solution of $CaCl_2$ (0.25M).

Microemulsion (water in oil) composition is:

- Igepal CO 520 solution (0.15M) 1 g
- NaOH (0.5M) and $CaCl_2$ (0.25M) aqueous solution 25 μ L (w=2)

20 Water/surfactants molar ratio ranging (molar ratio w=water/surfactant) from 1 to 11.

Aqueous solution was added to oil phase/surfactant solution by a microsyringe.

The preparation was held at environmental (25°C). Analogous systems, isotropic,

transparent, and stable was obtained in a wider temperature range, 15-25°C.

Microemulsions have been equilibrated at 25°C for a week.

Synthesized particles, after filtration, washing, and drying have been dispersed in nonaqueous solvents, by vigorous stirring and/or with the aid of a homogeniser.

5 Procedures for application

The physico-chemical properties of the prepared dispersions make them very attractive for different application procedures in paper deacidification processes, such as:

- spraying,
- 10 • immersing,
- brushing,
- mass-deacidification process.

Small particle dimensions allows using a sprayer without risks of hole occlusion.

The spraying method is preferred.

15 The complete immersion of paper sheet is possible also for longer period.

Aqueous deacidification methods, because of the strong aggressive effect of high pH, do not allow a long contact with paper sheet, commonly up to 20 minutes. This produces only a poor deacidification effect.

Moreover the basic suspensions according to the invention can be used also for
20 the consolidation of porous materials as for example stones, plasters building materials and similar.

Claims

- 1) Basic suspension wherein the suspended particles have dimensions comprised between 10nm up to 2 μ m.
- 2) Basic suspensions according to claim 1 wherein the suspended particles have
5 dimensions comprised between 50nm up to 500nm.
- 3) Basic suspensions according to claims 1 and 2 wherein the suspended particles are basic oxides or hydroxides or carbonates or their mixture.
- 4) Basic suspensions according to claim 3 wherein the suspended basic oxides are chosen in the group consisting of: Li₂O, Na₂O, K₂O, MgO, CaO, SnO, SnO₂,
10 PbO, Pb₂O Pb₂O₃, BiO, Bi₂O₃, Sb₂O₃ or their mixtures.
- 5) Basic suspensions according to claim 3 wherein the suspended basic hydroxides are chosen in the group consisting of : LiOH, NaOH, KOH, Mg(OH)₂, Ca(OH)₂, Al(OH)₃, Sn(OH)₂, Sn(OH)₄, Pb(OH)₂, Bi(OH)₃, Sb(OH)₃ or their mixtures.
- 15 6) Basic suspensions according to Claim 3 wherein the suspended basic carbonates are chosen in the group consisting of: Li₂CO₃, Na₂CO₃ deca-hydro, Na₂CO₃, K₂CO₃, MgCO₃, CaCO₃, PbCO₃, anhydro and basic, Bi₂O₂CO₃ or their mixtures.
- 7) Basic suspensions according to Claims 1 – 6 wherein the solvents are chosen
20 in the group consisting of: water, ethyl ether, acetone and alcohols and their mixtures.
- 8) Basic suspension according to claim 7 wherein the alcohols are chosen in the group consisting of: methanol, ethanol, 1-propanol, 2-propanol, butanol, pentanol, and their mixtures.

- 9) Basic suspension according to Claims 1 – 8 consisting of: $\text{Ca}(\text{OH})_2$ hydroxide particles suspended in 1% water and 99% 1-propanol or 2-propanol (w/w).
- 10) Process for the preparation of the suspensions according to Claims 1 – 9 by vigorous stirring of the particles to be suspended in the appropriate solvent (or solvents mixture), if necessary with the aid of a sonicator or ultra-sonicator or with the aid of a homogeniser
- 11) Process according to Claim 10 wherein the particles to be suspended are obtained by high temperature homogeneous phase reaction.
- 12) Process according to Claim 10 wherein the particles to be suspended are obtained by slaking of the oxides.
- 13) Process according to Claim 10 wherein the particles to be suspended are obtained by mixing two water in oil microemulsions, giving a low solubility salt in nanosized aqueous core.
- 14) Use of the suspension according to claims 1- 9 in paper deacidification processes, as neutralising agent and also as alkaline reservoir.
- 15) Process for paper deacidification wherein suspensions according to claims 1 - 9 are applied to the papers to be deacidified by: spraying, immersing, brushing, or by mass-deacidification process.
- 16) Use of the suspensions according to Claims 1 – 9 in processes for the consolidation of porous materials.

INTERNATIONAL SEARCH REPORT

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According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 D21H		
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Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 001 084 A (ZFB ZENTRUM FUER BUCHERHALTUNG) 17 May 2000 (2000-05-17) column 6, line 55 -column 8, line 22; claims 1-6	1-8, 14, 15 13
Y	EP 0 543 372 A (SYREMONT SPA) 26 May 1993 (1993-05-26) claims 1-15; examples 1-4	13
Y	EP 1 134 302 A (CONSORZIO INTERUNIVERSITARIO P) 19 September 2001 (2001-09-19) claims 1-13; examples 1,2	13
X	US 4 522 843 A (KUNDROT ROBERT A) 11 June 1985 (1985-06-11) claims 1-24; examples 6,7	1,3-5,7, 8,14,15
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Karlsson, L</div>

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PCT/EP 02/00319

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 080 448 A (BURD JAMES E ET AL) 27 June 2000 (2000-06-27) column 3, line 16 -column 4, line 48; claims 1-17	1,4,5, 14,15
X	WO 99 01377 A (KEMPRO ITALIANA S R L ;TODARELLO FRANCESCO (IT)) 14 January 1999 (1999-01-14) claims 1-16	1,7
X	US 6 235 150 B1 (SCALLAN ANTHONY M ET AL) 22 May 2001 (2001-05-22) claims 1-26	1
A	US 6 025 034 A (BOLAND ROSS F ET AL) 15 February 2000 (2000-02-15) claims 1-13; examples 1-8	1-16
A	EP 1 111 128 A (UNIV CATALUNYA POLITECNICA) 27 June 2001 (2001-06-27) the whole document	1-16
A	US 5 433 827 A (PAGE DEREK H ET AL) 18 July 1995 (1995-07-18) the whole document	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP 02/00319

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1001084	A	17-05-2000	DE	19921616 A1	18-05-2000
			EP	1001084 A2	17-05-2000
EP 0543372	A	26-05-1993	IT	1252006 B	27-05-1995
			CA	2083460 A1	21-05-1993
			EP	0543372 A1	26-05-1993
			JP	6015161 A	25-01-1994
EP 1134302	A	19-09-2001	EP	1134302 A1	19-09-2001
US 4522843	A	11-06-1985	CA	1235555 A1	26-04-1988
			FR	2578198 A1	05-09-1986
			GB	2171122 A , B	20-08-1986
US 6080448	A	27-06-2000	AU	743868 B2	07-02-2002
			AU	3205099 A	25-10-1999
			CA	2326998 A1	14-10-1999
			EP	1068395 A1	17-01-2001
			JP	2002510758 T	09-04-2002
			WO	9951819 A1	14-10-1999
			US	6342098 B1	29-01-2002
WO 9901377	A	14-01-1999	IT	RM970391 A1	04-01-1999
			AT	208739 T	15-11-2001
			AU	8802998 A	25-01-1999
			CN	1261860 T	02-08-2000
			DE	69802538 D1	20-12-2001
			DE	69802538 T2	23-05-2002
			WO	9901377 A1	14-01-1999
			EP	0996588 A1	03-05-2000
US 6235150	B1	22-05-2001	AU	2708799 A	18-10-1999
			BR	9909003 A	28-11-2000
			CA	2324459 A1	30-09-1999
			WO	9949133 A1	30-09-1999
			EP	1068391 A1	17-01-2001
			JP	2002507675 T	12-03-2002
US 6025034	A	15-02-2000	US	2001004473 A1	21-06-2001
			US	2002031658 A1	14-03-2002
			CA	2237588 A1	22-05-1997
			CN	1175984 A	11-03-1998
			EP	0866885 A1	30-09-1998
			WO	9718341 A1	22-05-1997
EP 1111128	A	27-06-2001	ES	2151835 A1	01-01-2001
			ES	2151836 A1	01-01-2001
			AU	5290699 A	28-02-2000
			BR	9912591 A	16-10-2001
			EP	1111128 A2	27-06-2001
			WO	0008250 A2	17-02-2000
US 5433827	A	18-07-1995	CA	2138445 A1	22-06-1995